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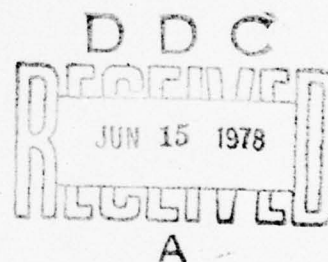OXIDATIVE STABILIZATION OF ACRYLIC FIBERS.   I.   OXYGEN

UPTAKE AND GENERAL MODEL

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ABSTRACT

The mechanism of oxidative stabilization of acrylic fibers is characterized by two limiting cases which are determined by the fiber chemistry, the reaction conditions, and the diameter of the filament. These limiting cases correspond to diffusion-limited and reaction-limited kinetic processes. Although the chemistry of stabilization is too complex to specify, the various reactions are separated into two categories: those which occur prior to or concurrently with polymerization of the nitrile groups, called "prefatory reactions"; and those which occur subsequent to nitrile polymerization, called "sequent reactions". Under conditions which allow the prefatory reactions to occur significantly before the sequent reactions, the diffusion of oxygen to reactive sites is limited by previously oxidized material; and the fiber shows a typical two-zone morphology. Under conditions where the prefatory and sequent reactions occur sequentially, the overall stabilization process is limited by the rate of the prefatory reactions; but a skin is established at the fiber surface which acts as an oxygen barrier. Data from a variety of sources, including oxygen analysis, microscopic examination, fiber residue after etching, tension developed in fibers held at constant length, and small angle X-ray patterns, are cited as evidence for the two limiting cases.

I. INTRODUCTION

The conversion of acrylic fibers into carbon or graphite fibers normally requires two or three processing steps: a slow thermal oxidation to stabilize the fibers prior to further treatment, carbonization in an inert atmosphere to eliminate the bulk of the heteroatoms, and a rapid high-temperature heat treatment in an inert atmosphere to eliminate the remaining heteroatoms and to develop the final carbon morphology. The high-temperature treatment is carried out either in the range of 1500 C or less to form high strength carbon fibers or in the range approaching 2800 C to form high modulus fibers. The carbonization step is generally used if only a modest degree of stabilization is achieved; with more extensive stabilization, the carbonization step may be omitted. The process of stabilization has been the subject of much study because it is costly and involves a number of chemical reactions which are poorly understood.

If an acrylic fiber is rapidly heated to the vicinity of 300 C-- the exact temperature depending on the heating rate, composition, bulk density, heat transfer conditions, environmental conditions (vacuum, inert gas, air) etc.--a destructive exotherm occurs with an attendant loss of weight and the generation of volatile gases, liquids, and waxes. To maintain good high temperature properties and to increase the yield of solid material, the destructive exotherm must be avoided and the chemical reactions controlled so that the properties of the final material are satisfactory. This is accomplished by heating the fibers at moderate temperatures in an oxidizing atmosphere, a process carried out under tension to provide desirable mechanical properties in

the final product. Detailed studies of the reactions occurring during this oxidative stabilization have been hampered by the fact that the stabilized material cannot be examined by the usually-powerful techniques of physical-organic characterization.

Most studies of stabilization have been concerned with the nature of the exotherm (1-4), changes in length which occur as the fibers undergo stabilization (5-7), changes in infrared adsorption (8-11) chemical analysis (12-13), or microscopic examination (14-15). A large variety of structures have been proposed for the stabilized material. These are based largely on the interpretation of rather broad, indistinct infrared bands. Few confirmatory results, based on alternative techniques or on the similarity of reactions in model systems, are available. The suggested structures, interpretations and processes are discussed in recent reviews (16, 17).

The area of stabilization phenomena is further characterized by a state of confusion and conflicting results because of a lack of characterization of the precursor (copolymer composition, cross-sectional configuration and area, post-spinning conditions and microstructure) and the variety of process conditions which are employed in stabilization.

Watt & Johnson (14) have recently shown that different phenomena can be observed during stabilization at a given temperature, depending on the copolymer composition. In particular, a commercial 3-denier (0.33 mg m^{-1}) fiber which contains a weak acid comonomer exhibits the following phenomena when heat treated in air at 230 C:

1. For stabilization times greater than a critical value, the fiber has a cross-section which consists of a dark rim and a cream-colored core. This is denoted as a two-zone morphology. The radius of the cream-colored core decreases linearly with the square root of time (18) for nearly all times where a distinct rim-core structure is observed.

2. The oxygen content of the fiber increases as the square root of time for nearly all times where a distinct rim-core structure is observed.

In contrast, Watt & Johnson showed that a commercial 1.8 denier (0.2 mg m^{-1}) fiber which did not contain a weak acid comonomer, displayed the following features when subjected to the same heat treatment conditions:

1. The fiber gradually increases in coloration throughout the cross-section as the time of stabilization increases. This is denoted as a single zone morphology.

2. The fiber combines with oxygen more slowly than the fiber containing the weak acid; the oxygen uptake of the fiber appears to speed up slightly with increasing time.

If, however, the fibers free of weak acid are subjected to a heat treatment in an inert atmosphere or vacuum (for, e.g., 6 hr. at 230 C in vacuum) prior to oxidation in air, the interior morphology and the curve of oxygen uptake vs. time both resemble the behavior of the fibers containing a weak acid.

The dark outer rim of the partially-stabilized fiber containing a weak acid or given a pre-treatment in an inert atmosphere (both treatments

being carried out on 3-denier fibers at 230 C) has been suggested to be oxygen-rich (19) or oxidized (14) relative to the core material. Watt draws the conclusions that a ladder polymer is formed prior to oxidation, a conclusion reached by Fitzer and Muller based on DTA measurements (3).

Previous work on oxidative stabilization can be summarized as follows: stabilization of a 3-denier fibers which contain a weak acid comonomer, carried out in air at 220-230 C, is limited by the diffusive transport of oxygen (13-14). Similar fibers which do not contain a weak acid comonomer, when stabilized under similar conditions, exhibit behavior limited by reaction rate (14). These results are, however, expected to change with the denier of the fiber and the temperature of stabilization.

A set of three papers will be presented which provide further insight into the stabilization of acrylic fibers. In the present paper (Part I), data derived from oxygen analysis, the examination of fiber cross-sections, and examination of solution-etched fibers, as well as the results of the papers to follow, are presented to elucidate the mechanism of stabilization. The second paper is concerned with small angle X-ray scattering and electron microscope studies of stabilization, together with a model of the morphology of acrylic fibers. The third paper describes the dynamics of the behavior of fibers during oxidative stabilization and follows the variation of tension in the fibers when stabilized at constant length and the instantaneous variations in local fiber velocity as a function of time as a fiber moves continuously and at constant overall velocity through a stabilization furnace.

II. EXPERIMENTAL PROCEDURE

(a) Materials

Three commercial acrylic fibers and one experimental fiber were employed in this work; their characteristics are summarized in Table I. They are described in these reports by a letter taken either from the trade name or from the supplier. It is not intended to rank these fibers by the relative efficiency of their stabilization, but rather to examine how different compositions and process variables affect stabilization. Only one of the fibers contains an acid comonomer (fiber C); the other three do not (fibers M, O, & D). Two fibers were prepared by wet spinning (fibers C & M); the other two by dry spinning. Fiber C was spun from an inorganic salt-water solution, whereas the others were spun from organic solvents.

(b) Elemental Analysis

The oxygen contents of fibers were determined by neutron activation analysis. Fiber samples were wrapped around a brass U-frame and then heat-treated for various times in a circulating air oven. The material near the frame was discarded, and the remaining fiber was flushed for two days with dry forming gas (5 pct. hydrogen, 95 pct. nitrogen) at 20 C and then sealed in ampules supplied by the analysts. Care was taken to exclude air and moisture from the ampules.

(c) Examination of Fiber Cross-Sections

Heat treated fibers were mounted in a thermosetting polyester, cut to 1-5 μm sections with an LKB ultramicrotome, immersed in oil, and examined under a Zeiss Universal Research Microscope using transmitted

light. Whenever a two-zone morphology was observed, the thickness of the oxidized zone was measured with a Filar eyepiece.

(d) Acrylic Solvents

To examine the effects of heat treatment, fiber samples were immersed either in 50 wt. pct. aqueous sulfuric acid solution at reflux for 24 hours or in boiling dimethyl formamide (DMF) for 3 min. On removal from the etching liquids, the fibers were washed in distilled water, allowed to dry in air, coated with a conductive layer of gold, and examined in a Cambridge Stereoscan scanning electron microscope (SEM).

These etching conditions were chosen because previous work (20) indicated that the sulfuric acid treatment would erode both the untreated virgin acylic fibers and fibers heat treated in an inert atmosphere, but sulfuric acid would not attack material which was completely stabilized in air. DMF, on the other hand, will readily dissolve virgin acrylic material, but not material heat treated for prolonged times in either air or vacuum.

III. RESULTS

The oxygen contents of 1.2 denier (0.13 mg m) fiber M and 3.8 denier (0.42 mg m) fiber C are shown in Fig. 1 as a function of heat treatment time in air at 220 C. The oxygen uptake of fiber C has a parabolic time dependence, whereas the oxygen uptake of fiber M is much slower, increasing linearly with time.

Examination of the fiber cross-sections shows that 3.8 denier fiber C, heat treated in air at 230 C, is characterized by a two-zone

morphology for times ranging from about 8 min. to about 1400 min. For times shorter than 8 min., no evidence of a two-zone structure is seen. At about 8 min. such a structure becomes visible, with the boundary between the zones located at about half the fiber radius. For the next 600 min., the mantle (outer-zone) thickness increases approximately linearly with the square root of time. This suggests that diffusive transport of oxygen is rate-controlling. For stabilization times longer than about 600 min. (Fig. 2), a slight acceleration in the rate of increase of the outer rim thickness is noted. This is very likely due to the geometrical effects of radially-inward diffusion. By 1400 min. the fibers are totally black.

Examination of the other fibers (M, O & D), with sizes in the 1-4 denier range shows that the fibers uniformly darken--from the original white, through yellow, orange, brown, and eventually to black--with increasing heat treament time in air at 220-230 C. This, coupled with the linear rate of increase of oxygen content, suggests that the stabilization process is reaction-rate limited, at least for the temperature and fiber deniers considered--but could simply reflect the morphological characteristics of the fibers (26, e.g.).

When the fiber denier and/or the reaction temperature is varied, the behavior can be changed for any of the four fibers. For example, 3-denier fiber C at 180 C is typified by a single-zone cross-section, while 3-denier fiber O at 260 C and 8-denier (0.89 mg m^{-1}) fiber M at 250 C are characterized by the two-zone morphology. The effect of denier

on the uptake of oxygen is illustrated by the data in Fig. 3 on Fiber
N at 250 C. The data indicate that the oxygen concentration in the
fibers after a given time of treatment decreases with increasing denier.

A scanning electron micrograph of a section of 3-denier fiber C
following partial stabilization at 230 C and sulfuric acid etching
is shown in Fig. 4. A hollow tube of stabilized material is present;
the inner core of material has been eroded. Fig. 5 shows a corresponding
micrograph of partially stabilized (again, 230 C) and etched 3-denier
fiber M. In this case, the bulk of the fiber has been attacked at various
points distributed uniformly across the cross-section, and the surface or
skin of the fiber has remained intact indicating its composition is that
of stabilized material.

IV. DISCUSSION

As indicated above, a plethora of reactions and reaction products
have been suggested by various authors as occurring during the stabilization
process. Since it is not yet possible to establish in detail which
reactions occur in the various stages of stabilization, it is proposed to
divide the stabilization process into two stages, much like Fitzer (3) and
Watt (14). The two stages will be used to explain the different cross-
section morphologies observed for fibers C and M when stabilized under
similar conditions.

The first group of reactions are called "prefatory" and those that
follow "sequent". In this context, prefatory reactions are those which

are involved in the initiation and polymerization of nitrile groups to form a reddish-brown chromophore. Oxidative reactions may be involved in the production of hydroperoxides, carboxylates, and other active groups--all of which act as initiators for nitrile polymerization. Nitrile polymerization can form a polyamine chain of the type suggested by Grassie (8), or the polyamine chain of the type proposed by Johnson et al. (2). Whatever combination of chemical species are present at the end of the prefatory stage (if sequent reaction do not occur simultaneously), the material is colored reddish-brown rather than black, is etched by sulfuric acid, and will burn in air when exposed to the flame of a match. Sequent reactions (also exothermic) occur when the products of the prefatory reactions are exposed to oxygen: the reddish-brown color rapidly turns black; the black material is not etched by sulfuric acid, and will not burn when exposed to the flame of a match. These two stages of the overall stabilization process are designated prefatory and sequent, and are used to describe the stage of stabilization without specifying in detail the underlying chemistry.

The basic thesis advanced here is that the fundamental processes involved in stabilization are similar for all acrylic fibers--but that the details of the process and the characteristics of the fibers at various stages of partial stabilization depend upon factors such as the temperature, fiber denier and fiber chemistry. This thesis has significant implications for processing acrylic fibers of various types, and will be supported by examples which illustrate the limiting cases of stabilization behavior.

When 3-denier fiber C, which contains a weak acid comonomer, is heated in air at 230 C the prefatory reactions occur quite rapidly throughout the fiber, since an initiator for nitrile polymerization is already present in the fiber. In the zone near the exterior of the fiber at treatment times of less than 8 minutes, the prefatory reactions occur in a region where oxygen can readily diffuse into the fiber, and sequent reactions start to occur simultaneously. Near the center of the fiber, prefatory reactions occur essentially in the absence of oxygen (save that which was dissolved or trapped in the fiber interior). Once the sequent reactions have occurred in the outer reaction zone, the diffusion of oxygen is further limited and the slow movement of the outer zone toward the fiber center is a result of oxygen diffusing through the reacted zone and reacting at an advancing front. If this explanation is correct, there should be distinct chemical differences between the core material and that near the fiber surfaces. Fig. 4 shows that the inner core of partially stabilized material which exhibits the two-zone morphology is removed by treatment in hot sulfuric acid.

Love et al. (19) examined by electron microprobe analysis a 3-denier sample of fiber O which had been heated for 1 hr. in air at 230 C after preliminary heat treatment in vacuum at 230 G for 1 hr. The fiber displayed a two-zone morphology; and the oxygen content was found to be higher in the dark-colored exterior of the fiber than in the cream-colored interior zone. In contrast, a similar sample of fiber O treated only in air for 1 hr. at 240 C displayed a fairly uniform coloration

across the cross-section. For the latter fiber, no significant differences in oxygen concentration (within the large scatter in the data) were found between the central region and the near surface region.

As indicated above, when the outer dark mantle is first perceived in fibers undergoing diffusion-limited reactions, it occupies some 40 or 50 percent of the radius. The classic diffusion-limited ($t^{1/2}$) kinetics are observed for times when the dark mantle is advancing toward the center of the fiber. During the initial period when the mantle is formed, the outer region darkens progressively with little or no apparent change in dimension. In cases where the diameter of the fiber is less than the first-seen thickness of the outer mantle, diffusion-limited kinetics should not be observed even at temperatures where such behavior is seen for larger fibers. The thickness of the first-seen outer mantle provides a measure of the scale on which the overall reaction becomes diffusion-controlled. It depends on both the diffusion coefficient of oxygen (which itself depends on the extent of reaction) and the kinetics of the slowest reactions (which very likely depend on the extent and kinetics of prior reactions).

The prefatory reactions occur whether the fiber is heated in an inert atmosphere, vacuum, an oxidizing atmosphere, and whether or not an initiator for nitrile polymerization is included in the precursor. The detailed character of these reactions as well as their rate are, however, expected to depend significantly upon the atmosphere, temperature of heat treatment, and polymer chemistry.

Grassie and McGuchan (1) have shown that weak acid comonomers have a strong initiating effect on nitrile polymerization, with polymers containing such comonomers undergoing the exothermic reaction and developing dark colors at lower reaction temperatures or at faster rates at a given temperature than polymers without the weak acid. Pretreatment in an inert atmosphere allows the prefatory reactions to get underway before exposure to oxygen, which takes part in the sequent reactions. Thus when the two zone texture is observed, the prefatory reactions are well established prior to the initiation of the sequent reactions. In this case, the rate of the overall stabilization process is limited by the transport of oxygen into the interior of the fiber and the process is termed diffusion-limited.

The measurements of Watt and Johnson (18) on the rate of thickening of the outer zone of 3 denier fibers heated in air at 220 C may be used together with a treatment of the sequent reactions as a

tarnishing process (22) to estimate the diffusion coefficient of oxygen through the reacted material. This treatment, together with the assumptions employed therein, are outlined in Appendix A. The results indicate a diffusion coefficient, D_{RM}:

$$D_{RM} \sim 2 \times 10^{-12} \text{ cm}^2 \text{ sec}^{-1} \tag{1}$$

This value is appreciably smaller than the diffusion coefficient of oxygen in PAN fibers reported by Allen (23). Allen obtained, for a temperature of 50°C:

$$D_{PAN} \sim 6 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1} \tag{2}$$

Since the diffusion coefficient in the reacted material at 50 C is expected to be appreciably smaller than its value at 220 C, the difference between reacted material and precursor fiber is larger than the indicated factor of 300. In this light, since PAN itself has notably good resistance to oxygen transport, the reacted material must be regarded as having outstanding barrier properties.

When 3 denier acrylic fibers which do not contain a catalyst for the prefatory reactions are heated in air at 230 C, the prefatory and sequent reactions seem to occur sequentially and simultaneously throughout the interior of the fiber; and the overall rate of stabilization is limited by the rate of the prefatory reactions. This may be termed a reaction-limited process.

The two limiting cases of the stabilization process--diffusion-controlled and reaction-controlled--are observed in all types of acrylic fibers. The observation of a particular limiting case depends upon temperature, time, fiber chemistry and denier. For example, small denier, low temperatures, and the absence of a weak acid comonomer favor observation of reaction-controlled kinetics. In contrast, diffusion-controlled kinetics are favored by large denier, high temperatures and the presence of catalyst for prefatory reactions. Diffusion-controlled kinetics can also be observed by heat treating fibers not containing a catalyst for prefatory reactions under inert conditions prior to their treatment under oxodizing conditions.

The rate of stabilization cannot be completely explained by the two extremes of diffusion-limited and reaction-limited kinetics. Under conditions where the single-zone morphology is observed there remains a decrease in the rate of oxygen uptake with fiber diameter, Fig. 3, which suggests a process that limits the flux of oxygen into the fiber. Reexamination of the acid-etched fiber, Fig. 5, indicates that although the interior of the fiber has been eroded, the exterior or skin is intact. The skin has resisted the sulfuric acid treatment, indicating that it may be composed of stabilized material which acts as an oxygen barrier. If this is correct, then the rate of oxygen uptake should vary directly with the surface---to-volume ratio. That is, the rate of oxygen uptake should be proportional to the surface area per unit volume, and hence to $(\text{denier})^{-1/2}$. A test of this relation is provided by the data in Fig. 6, which indicates reasonable agreement with the suggested relation.

From the data in Fig. 6, a rough estimate of the skin thickness, ℓ, can be obtained. From Fick's first law:

$$J = D(C_s - C_i)/\ell \qquad (3)$$

where J is the flux of oxygen into the fiber, and equals the rate of oxygen uptake (obtained from Fig. 1) divided by the cross-sectional area of the fiber; C_s is the oxygen concentration at the surface as defined in the Appendix; C_i is the free oxygen concentration inside the fiber which is assumed to be negligible; and D is the diffusion coefficient of oxygen through the skin. With these approximations, and taking D as the value obtained for the diffusion of oxygen through oxidized Fiber C [Eq. (1) above], ℓ is calculated as approximately 1 µm. This value for ℓ in reasonable agreement with that measured from Fig. 5, about 0.4 µm.

The origin of the skin is unclear. Because of the high concentration of oxygen at the surface of the fiber, prefatory and sequent reactions may occur at an accelerated rate, thus establishing a barrier to the transport of oxygen into the fiber. Alternately, the surface regions of uncollapsed wet-spun acrylic fibers are known to be more dense than the cores of the fibers (24, 25), and this material may form the skin observed in the stabilized fibers.

The evidence presented thus far for the occurrence of diffusion-limited and reaction-limited extremes in the oxidative stabilization of acrylic fibers is based on both microscopic measurements and chemical analyses. In the reaction-limited regime, it is assumed that oxygen can diffuse through regions which have not undergone prefatory or sequent reactions in

a time which is short compared with the time required for these reactions
to occur. That is, both reactions occur sequentially at various sites
distributed throughout the bulk of the fiber. Within the resolution of
the light microscope, these sites are uniformly distributed in the
fiber.

If the density of material at different stages of the reaction
process differs from that of the starting material, and if the reactions
take place at a large number of individual sites, then their occurrence
should produce an increase in the small angle X-ray scattering (SAXS)
from the fibers. Three such SAXS studies of acrylic fibers undergoing
reaction-limited stabilization have been carried out previously (21,27,28).
The results indicate the development and subsequent annihilation of an
intense SAXS peak in the course of stabilization. This peak can be
associated with the presence of many heterogeneities distributed through-
out the interior of the fiber. Evidence has been presented (26) for
a fairly definite separation between adjacent heterogeneities along the
fiber axis, which can be related to morphological characteristics of
the precursor acrylic fibers.

In the case of stabilization under diffusion-limited conditions,
the heterogeneities associated with the sequent reactions might be
viewed as occurring primarily in a relatively narrow zone at the
advancing front between the prefatory-reacted and the sequent-reacted
regions. The heterogeneities associated with prefatory reactions are
expected to be distributed throughout the fiber; and during the initial

formation of the outer dark mantle, heterogeneities associated with sequent reactions should also be distributed throughout a sizable volume of the fiber.

SAXS studies of fiber C treated under conditions of diffusion-controlled stabilization exhibit a transitory maximum in scattering similar to that observed for fiber M treated under conditions of reaction-controlled stabilization. In both cases, the angular location of the maximum in intensity corresponds to a Bragg-law spacing of about 100Å. The times of appearance and disappearance of the SAXS maximum are, however, much shorter in the case of fiber C. The transitory maximum is also observed in fiber C when it is heat treated in an inert atmosphere. This last result indicates that sequent reactions are not the primary cause of the small angle scattering. It should also be noted that the most intense scattering from fiber C treated in air occurs at times which are considerably longer than those required to establish the dark outer mantle (at times well within the range of diffusion-limited reactions).

Paper II in the present series (26) suggests that the fibrils in polyacrylonitrile fibers consist of ordered rods which form a lyotropic amphiphilic middle phase liquid crystal--i.e., layers of more ordered rods interspersed with layers of less-ordered amorphous material. It is suggested that the prefatory reactions occur more rapidly in one of these phases (very likely the amorphous phase), thereby establishing

the regions differing considerably in electron density. The dimensions

of the suggested structural inhomogeneities are consistent with those

inferred from the angular position of the SAXS maximum. Once the

reactions occur to an appreciable extent in the second phase, the density

differences between different regions in the fibers will decrease and

the SAXS will show a corresponding decrease. Since the largest SAXS

in fiber C stabilized under diffusion-controlled conditions occurs well

after the outer mantle is established, it is suggested that prefatory

reactions are continuing in the fiber even after the outer mantle is

established, and consequently that the sequent reactions also occur

in the outer mantle subsequent to its formation.

When fibers are stabilized at constant length, the tension developed in the fibers changes as a function of time. By altering the atmosphere in the stabilization oven, the prefatory reactions can be separated from the sequent reactions: the latter do not occur in the absence of oxygen, and the fiber tension increases slowly with time. When oxygen is present, the characteristics of the development of tension vary with the nature of the stabilization process. Paper III in the present series (29) shows that fibers undergoing diffusion-limited stabilization develop tension as soon as the fibers reach the reaction temperature (approximately ten minutes), whereas fibers undergoing reaction-limited stabilization develop tension far more slowly.

V. CONCLUSIONS

Two different limiting conditions of stabilization, designated diffusion-limited and reaction-limited, have been noted to occur in the heat treatment of acrylic fibers. The role of oxygen uptake, the texture of the fiber cross-section, the fiber residue after etching, the tension developed in fibers held at constant length, and the small angle X-ray scattering pattern are characteristics which can be used to differentiate between the two limiting conditions.

The reactions which fibers undergo during stabilization have been classified into two groups: Those that lead up to and include polymerization of the nitrile groups are called prefatory reactions; and those that involve the reaction of polymerized nitrile groups with oxygen are called sequent reactions.

The diffusion-limited condition is illustrated by the formation of a two-zone morphology in the fiber: a dark outer mantle surrounding a light colored core. During stabilization, the interface between mantle and core moves toward the fiber center. In this case, prefatory reactions preceed the sequent reactions, and the movement of the interface is associated with diffusion of oxygen through already-stabilized material to the interface where sequent reactions occur. The uptake of oxygen varies linearly with the square root of time from the time when a distinct mantle-core boundary is first observed.

Under reaction-limited stabilization conditions, prefatory reactions occur rapidly at the fiber surface and less rapidly at selected but uniformly distributed locations through the fiber interior. A skin is formed on the fiber surface which limits the flux of oxygen into the fiber, but once oxygen has permeated the skin, it is realtively free to diffuse in the unreacted regions and to initiate the prefatory and sequent reactions. The uptake of oxygen is linear with time.

ACKNOWLEDGMENTS

APPENDIX A

Evaluation of Diffusion Coefficient of Oxygen through

Stabilized Material

The analyses of Crank (23) for tarnishing reactions can be used to estimate the diffusion coefficient of oxygen through stabilized material. According to this analyses, the diffusion coefficient can be expressed:

$$D = (\frac{1}{2\alpha} \cdot \frac{X}{t^{1/2}})^2 \tag{4}$$

where α is a dimensionless variable related directly to $g = C_s/W\xi$, (see Ref. 23), in which ξ is the density of the oxidized material, W is the mass fraction of oxygen in the stabilized material, and C_s is the concentration of oxygen adsorbed onto the surface in grams per volume of oxide. Based on published data (9, 18), W is about 0.20; and approximating the molecular weight of the stabilized material as 120 gms mole^{-1} based on the Watt (14) model of the stabilized fiber, $C_6H_4N_2O$, g is estimated as about 0.26. Using this value of g with Crank's analysis, $\alpha \stackrel{\sim}{=} 0.39$. Applying Eqn. (4) with $\alpha = 0.39$ the data of Watt and Johnson (18) on oxygen pickup in fibers of type C at 220 C, one obtains:

$$D \simeq 2 \times 10^{-12} \text{ cm}^2/\text{cm}$$

In making this calculation, the following assumptions and approximations have been made: (1) Fickion diffusion through a homogeneous medium; (2) a diffusion coefficient independent of concentration; and (3) C_s approximately equal to the concentration of oxygen in air.

REFERENCES

1. N. Grassie and R. McGuchan, Europ. Polym. J. $\underline{6}$ (1970) 1277; $\underline{7}$ (1971) 1091; $\underline{7}$ (1971) 1357; $\underline{7}$ (1971) 1053; $\underline{8}$ (1972) 243; $\underline{8}$ (1972) 257; $\underline{8}$ (1972) 865; $\underline{9}$ (1973) 113; $\underline{9}$ (1973) 507.

2. J. W. Johnson, W. Potter, P. G. Rose, and G. Scott, Brit. Polym. J. $\underline{4}$ (1972) 527.

3. E. Fitzer, and D. J. Muller, ACS Polym. Preprints $\underline{14}$ (1973) 397.

4. E. Fitzer and D. J. Muller, Makromol. Chem. $\underline{144}$ (1971) 117.

5. O.P. Bahl and L. M. Manocha, Angew. Makromol. Chem. $\underline{48}$ (1975) 145.

6. D. J. Muller, E. Fitzer and A.K. Fiedler, Proc. Int. Carbon Fibers Cinf., Plastics Inst., London (1971) 10.

7. W. Watt and W. Johnson, Applied Polymer Symposia $\underline{9}$ (1969) 215.

8. N. Grassie, and J. N. Hay, J. Poly. Sci. $\underline{56}$ (1962) 189.

9. A.J. Clarke, and J.E. Bailey, Nature $\underline{243}$ (1973) 146.

10. S.I. Stupp and S.H. Carr, J. Polymer Sci., Polym. Phys. Ed. $\underline{15}$ (1977) 485.

11. B. Danner and J. Meybeck, Proc. Int. Carbon Fibers Conf., Plastics Inst. London (1971) 36.

12. K. Miyamichi, M. Okamoto, O. Ishizuka, M. Katayama, Sen-i Gakkaishi $\underline{22}$ (1966) 538 (Trans. available from Royal Aircraft Establishment, U.K.).

13. W. Watt and J. Green, Proc. Int. Carbon Fibers Conf., Plastics Inst., London (1971) 23.

14. W. Watt and W. Johnson, Nature $\underline{257}$ (1975) 210.

15. R.H. Knibbs, J. Microscopy $\underline{94}$ (1971) 273.

16. P.J. Goodhew, A.J. Clarke and J.E. Bailey, Materials Sci. and Eng. $\underline{17}$ (1975) 3.

17. L.H. Peebles, Jr., Encyclopedia of Polymer Science and Technology, Supplementary Vol. #1 (Wiley, 1976) 1.

18. W. Watt and W. Johnson, Proc. 3rd Conf. Ind. Carbon and Graphite, Soc. Chem. Ind., London (1970), 417.

19. G. Love, M.G. Cox and V.D. Scott, Mat. Res. Bull. $\underline{10}$ (1975) 815.

20. S.B. Warner, Sc.D. Thesis, MIT (1976).

21. G. Hinrichsen, J. Appl. Polym. Sci. $\underline{17}$ (1973) 3305.

22. J. Crank, Mathematics of Diffusion (Oxford Univ. Press, 1956), ch. 7.

23. S. Allen, Ph.D. Thesis, North Carolina State University (1975).

24. J.P. Craig, J. P. Knudsen, and V.F. Holland, Textile Res. J. $\underline{32}$ (1962) 435.

25. J.H. Dumbleton and J. Bell, J. Appl. Polym. Sci. $\underline{14}$ (1970) 2402.

26. S.B. Warner, L.H. Peebles, Jr. and D.R. Uhlmann, "Oxidative Stabilization of Acrylic Fibers. II. Morphology of Polyacrylonitrile."

27. M.E. Fillery and P.J. Goodhew, Nature Physical Science $\underline{233}$ (1971) 118.

28. C.N. Tyson, Nature Physical Science $\underline{229}$ (1971) 121.

29. S.B. Warner, L.H. Peebles, Jr. and D.R. Uhlmann, "Oxidative Stabilization of Acrylic Fibers. III. Stabilization Dynamics."

FIGURE CAPTIONS

Figure 1 - Oxygen uptake of fiber M and fiber C as a function of time at 220C.

Figure 2 - Mantle thickness vs time$^{1/2}$ for fiber C heat treated in air at 230C.

Figure 3 - Oxygen uptake of various deniers of fiber N (obtained by varying the draw ratio) as a function of time at 250 C.

Figure 4 - Scanning electron micrograph of fiber C after stabilization in air at 240C for 80 min. then etched in aqueous sulfuric acid at reflux.

Figure 5 - Scanning electron micrograph of fiber M treated by conditions given in Fig. 4.

Figure 6 - Oxygen uptake rate of fiber N at 250C as a function of surface to volume ratio expressed as (denier)$^{-1/2}$.

Table 1

Acrylic Fiber Data

Fiber Description	Manufacturer	Copolymer Composition	
M, N	Monsanto	7% Vinyl acerate	drawn experimental fibers
O	Du Pont	6% methyl acrylate	sweater grade, type 42, crimped
D	Bayer	homopolymer	Z twist
C	Courtaulds	6% methyl acrylate 1% itaconic acid	sweater grade, crimped

3 μm

3 μm